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An EXAFS Analysis of Trace Metals in Wood Pulp

A. Rudie (Inst. Of Paper Sci. and Tech.), G. Ow Yang, and D. Hunter (Savannah River Site)

Beamline(s): X18B, X19A

Introduction: The wood used as a raw material in production of paper contains trace levels of many metals. Although most are harmless, Calcium can accumulate to levels that cause mineral scale formation in the bleach plant, and iron can cause problems in bleaching. The project seeks to improve our understanding of the behavior of these metals in the pulping and pulp bleaching process by characterizing the molecular form or metal binding sites at various points in the process.

Methods and Materials: The EXAFS technique has been used to characterize calcium in unbleached pulp as it is received from the pulping process, and residual iron in partially bleached pulp. Pulp samples were prepared by pressing the pulps into a 13 mm diameter pellet. Reference samples were prepared by mixing suitable reagent grade materials with dextrose to obtain about 2% concentration of the target metal. These were then pressed into pellets using a KBr pellet press, or – in the case of iron, prepared as a powder distributed on Scotch tape for X-ray measurements in transmission. All calcium and barium data were collected on X-19A in fluorescence mode using a PIPs detector. Additional oriented EXAFS experiments were carried out on calcium samples by cutting pulped wood chips to align the wood fibers parallel to the beam, perpendicular to the beam and aligned towards the detector, and perpendicular to both the beam and the detector. Iron spectra were collected on X18B using the X-ray fluorescence and the 13 element Ge detector for dilute samples, and a PIPs detector for concentrated samples when data was collected in transmission.

Results: The calcium found in unbleached pulp is in the form of calcite particles estimated to be about 1 nm in diameter. In mineral calcite, each calcium is surrounded by 6 other calcium ions at ~3.6Å in the RSF. The EXAFS spectrum of calcium in unbleached pulp shows a similar feature at 3.6Å, but detailed analysis suggests each calcium is surrounded by just 3-4 other calcium ions. A single crystallite of one calcium surrounded by 6 others gives an average of 4.3 surrounding calcium ions and corresponds to a particle diameter of about 10Å. Experiments to determine if the crystals were oriented relative to the cellulose polymer (and wood fiber axis) indicate they are not oriented.

The iron of concern is what is referred to as hard-to-remove, or intractable iron. It is the iron that remains after wood pulp has been treated with dilute acid or a chelating agent, and is of concern because it decomposes peroxide into oxygen and water. Using EXAFS, iron has been found to be associated with the lignin portion of the wood polymer. It is bound to a site containing at least four organic oxygen atoms, and contains two additional waters of hydration. Current efforts are directed towards determining if the binding sites contain guaiacyl (2-methoxyphenol) or catechol (1,2-dihydroxybenzene) type monomers.

Conclusions: Demonstrating that calcium is in the form of calcite in brown stock pulp is useful in suggesting that bleaching processes operating at a pH above 8 will have few problems with mineral scale. It is also critical information for modeling the trace metals buildup in a bleach plant since the calcium will not go into solution until the pH drops below 8. Confirmation that iron is bound to a lignin site is critical in that it then will go into solution during the bleaching process (when the remaining lignin is removed). Since dissolved iron decomposes peroxide based bleaching agents, continued effort to control the residual iron is necessary in bleach plants that use hydrogen peroxide. Continued efforts to reduce pulp and paper mill effluents need to solve this residual trace iron issue if they are going to succeed.

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